



TITLE:

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CITATION:

Arimoto, Tateo ...[et al]. The charge-transfer interaction and successive thermal (2+2) cycloaddition of α , β -unsaturated ethers with tetracyanoethylene. The Review of Physical Chemistry of Japan 1974, 44(1): 25-37

ISSUE DATE:

1974-09-30

URL:

<http://hdl.handle.net/2433/46995>

RIGHT:

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN. VOL. 44, No. 1, 1974

THE CHARGE-TRANSFER INTERACTION AND SUCCESSIVE THERMAL (2+2) CYCLOADDITION OF α , β -UNSATURATED ETHERS WITH TETRACYANOETHYLENE

BY TATEO ARIMOTO and JIRO OSUGI

The systems of α , β -unsaturated ethers and substituted olefins with tetracyanoethylene (TCNE) give deeply colored 1 : 1 CT complexes immediately after mixing. Subsequently, the complexes react to form colorless 1, 1, 2, 2-tetracyano-cyclobutanes only in the case of the ethers. Equilibrium studies on the complex formations and kinetic studies on the successive thermal (2+2) cycloaddition reactions were made in such poor solvents as CH_2Cl_2 , CHCl_3 and CCl_4 in the temperature range 10–40°C by the spectrophotometric method.

TCNE-unsaturated ether and TCNE-olefin complexes exhibit gradual increases in stability with the increase of the double-bond substitution, in contrast with Ag^+ -unsaturated ether, Ag^+ -olefin and I_2 -olefin complexes where the complexes become more unstable with increasing substitution at the double bond. This tendency could be interpreted by considering that the electronic and steric effects of the substituents are mutually competing. Furthermore, there is significant difference in the substituent effect on the reactivity between the complex formation and the successive cycloaddition. The difference would be caused by the fact that the steric effect is more important in the activation process of the cycloaddition because the transition state seems much more rigid than the complex state. The cycloaddition reaction proceeds stereoselectively.

The experimental results were discussed on the basis of the extended Hückel molecular orbital (EHMO) theory and the molecular orbital correlation diagram.

Introduction

Since the end of the 19th century it had been known to chemists that two molecules with their valencies saturated interact to form a stable complex. Various theoretical speculations had been proposed for interpreting this phenomenon, until about 20 years ago Mulliken¹⁾ achieved real insight into the molecular nature of some type of the complex on the basis of quantum mechanics; Mulliken's theory is called "Charge-Transfer (CT) Theory". Since then the information on the thermodynamic behaviors of CT complexes have increased^{2,3)}. However, the practical role of CT complexes in the reaction has been carefully examined only in a few instances^{4,5)}, even though such complexes as

(Received March 26, 1974)

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Dewar's π -complex⁶⁾ and Wheland's σ -complex⁷⁾ are frequently postulated as intermediates or transition states.

Recently Williams *et al.*⁸⁾ found that TCNE cycloadds thermally to electron-rich olefins under mild conditions, but its mechanism has not been examined. For this purpose we studied the reactions of α, β -unsaturated ether and substituted olefin with TCNE^{9,10)}, which are thought to be the good models for investigating the possible role of CT complexes. These systems are so simple that the substituents on the double bond have considerably large effects on the NMR spectra, on the CT bands, and on the relative reactivities both in the complex formation and in the cycloaddition. The following two basic problems are discussed in this paper. First, how do the substituents affect the energy level and the electron distribution of the donor; practically its ionization potential and NMR spectrum? Secondly, how do the energy level and the electron distribution determine the reactivities both in the complex formation and in the successive reaction?

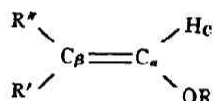


Fig. 1 α, β -unsaturated ether

Experimental

Materials

Propenyl ethyl ether (PEE), isobutenyl ethyl ether (IBEE), 1,2-diethoxyethylene, and *p*-methoxy-styrene were prepared by the known methods¹¹⁾. The other donor was commercially available. All the donors were purified by the method described elsewhere¹²⁾. TCNE was recrystallized from chlorobenzene three times, and then sublimed under high vacuum. The sublimate was colorless and its melting point was 200–202°C. Spectrograde CCl_4 was used without further purification. CH_2Cl_2 and CHCl_3 were purified by the usual method.

Apparatus and Procedure

Ultraviolet-visible spectra were measured with a Shimadzu UV-200 and a Hitachi EPU-2A spectrophotometer. Thermostated water was circulated around the quartz observation-cell compartment (optical

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path length is 10 mm) and the donor and acceptor solution reservoirs; the temperature was regulated within $\pm 0.2^\circ\text{C}$. The donor and acceptor solutions were mixed directly in the observation cell. The initial absorption measurements could be made within 6 sec. All kinetic and equilibrium experiments were carried out with the donor in large excess over the acceptor; the donor concentration, $(D)=0.2-1.6\text{ M}$ and the acceptor concentration, $(A)=ca.10^{-3}\text{ M}$. The cycloaddition reaction was followed by observing the CT band maximum and, if necessary, various wave lengths near this. The pseudo first order rate constant was obtained by Guggenheim's plot. The initial association constant was obtained by Benesi-Hildebrand (B-H) plot¹³⁾. In the case of reacting systems, we made use of the absorbance value obtained from the extrapolation of Guggenheim's plot to zero time in order to take the B-H plot.

NMR spectra were taken at 100 MHz using deuterioacetone and CCl_4 as solvents with TMS as an internal reference at room temperature.

Results and Discussion

Assignment of the new band

The maximum of the observed new band and H_C chemical shift of the donor are listed in Table 1. We can see that the effects of β -substituents are much larger than those of α -substituents on these

Table 1 The CT spectra with TCNE and H_C chemical shifts of the donors in CCl_4

	Donor	λ_{CT}	τ value of H_C
REACTIVE ^{a)}	vinyl 2-chloroethyl ether (V2-CIEE)	403 nm	3.64 ppm
	vinyl methyl ether (VME)	410	3.60
	vinyl ethyl ether (VEE)	428	3.70
	vinyl <i>n</i> -butyl ether (Vn-BE)	432	3.72
	vinyl isobutyl ether (Vi-BE)	436	3.74
	<i>cis</i> -propenyl ethyl ether (<i>cis</i> -PEE)	480	4.20
	<i>trans</i> -propenyl ethyl ether (<i>trans</i> -PEE)	480	3.90
	isobutenyl ethyl ether (IBEE)	518	4.42
	2,3-dihydro pyran	471	
	1,2-diethoxy ethylene	582	
	<i>p</i> -methoxystyrene	586	
NONREACTIVE ^{b)}	pentene-1	340	4.3
	pentene-2	404	4.7
	2-methyl-2-butene	467	4.9
	tetramethylethylene	562	
	cyclohexene	420	
	styrene	475	

a) "REACTIVE" indicates that the cycloadducts could be identified by the product analyses (IR, UV, NMR and elemental analysis).

b) "NONREACTIVE" indicates that the cycloadducts could not be identified.

13) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949)

spectra. The new band is assigned to the CT absorption band¹⁾ from the following reasons. First, as Mulliken's CT theory predicts, the plot of the frequencies of the new bands against the experimental ionization potentials of the donors¹⁰⁾ really shows a linear relationship in Fig. 2. Then, the complex

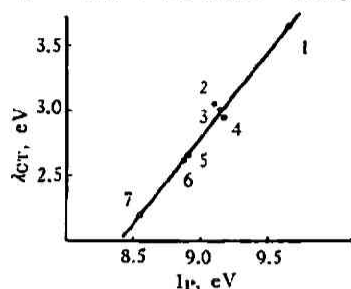


Fig. 2 Frequencies of the CT bands for some TCNE complexes plotted against the ionization potentials of the donors

1; pentene-1 2; pentene-2 3; VME
4; cyclohexene 5; 2-methyl-2-butene
6; styrene 7; tetramethylethylene

stoichiometry is found 1 : 1 from the continuous variation plot¹⁵⁾. Furthermore, the ¹H-NMR chemical shift of H_C and -OCH₂- in the complexed IBEE is about 0.1 ppm to the lower field in comparison with the isolated IBEE in CCl₄, and the other protons do not show any shift; these shifts probably suggest that partial charge would migrate from the donor to the acceptor. According to these results, it can be concluded that the appearance of the new band is due to the formation of 1 : 1 CT complex.

Complex formation equilibrium

The equilibrium constant of the complex formation, *K* and molar extinction coefficient, *ε* were determined by B-H plot as seen in Fig. 3. The values of *ε* do not vary among the donors used; 2000

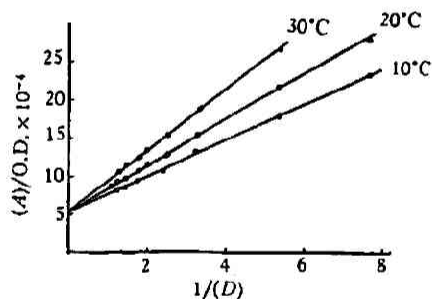


Fig. 3 Typical Benesi-Hildebrand plots
Donor: IBEE in CCl₄

±50 in CHCl₃ and 1400±100 in CCl₄. The heat and entropy of formation (ΔH° and ΔS°) are determined from the temperature dependence of *Kε* value, assuming *ε* has no temperature dependence, and using the equation $R \ln K\epsilon = -\Delta H^\circ(1/T) + \Delta S^\circ R \ln \epsilon$. The thermodynamic parameters obtained thus are listed in Table 2. The values of ΔH° and ΔS° are both negative and have magnitudes similar to those of common π - π complexes²⁾.

It is found that there are good linear relationships between the obtained values of log *K* and $\tilde{\nu}_{CT}$, and lines A and B have the same slope as seen in Fig. 4. According to Mulliken's simplified resonance theory¹⁶⁾ the wave function for the ground state (N) of a complex is generally expressed as Eq. (1).

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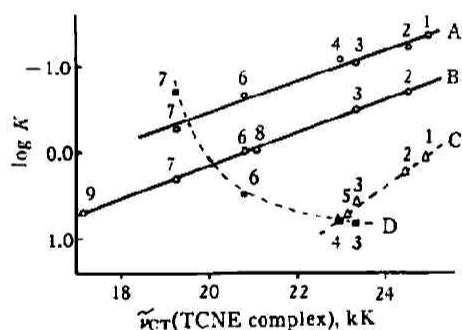
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Table 2 The thermodynamic parameters for the TCNE complex formation equilibria

Donor	K (1 mol ⁻¹)			ΔH° (kcal mol ⁻¹)	ΔS° (e. u.)	Solvent
	10°C	20°C	30°C			
IBEE	2.16	1.91	1.34	—	-3.9	CCl ₄ ^{a)}
	0.74	0.65	0.52	—	-3.0	CHCl ₃
<i>cis</i> -PEE ^{b)}	—	0.91	—	0.67	-2.9	CCl ₄
	0.24	0.21	0.18	—	-2.3	CHCl ₃
<i>trans</i> -60-PEE ^{c)}	—	0.18	—	—	—	CHCl ₃
VEE	—	0.33	—	0.27	-1.7	CCl ₄
	0.10	0.094	0.088	—	-1.0	CHCl ₃
Vi-BE	0.084	0.078	0.072	—	—	CHCl ₃
VME	—	0.073	0.071	—	—	CHCl ₃
V2-CIEE	—	—	0.05	—	—	CHCl ₃
styrene	—	0.93	—	—	—	CCl ₄
<i>p</i> -methoxystyrene	—	4.5	—	—	—	CCl ₄

a) 95 vol. % CCl₄-5 vol. % CH₂Cl₂b) and c) *cis*-PEE indicates the PEE containing 95% *cis* isomer and *trans*-60-PEE indicates the PEE containing 60% *trans* isomer, because the geometrical isomers of PEE could not be completely separated.Fig. 4 A plot of $\log K$ vs. the frequency of the CT band for some TCNE complexesA: TCNE at 30°C in CHCl₃B: TCNE at 20°C in CCl₄C: I₂ at 23°C in isooctaneD: Ag⁺ at 20°C in ethylene glycol

1; V2-CIEE 2; VME 3; VEE
 4; Vi-BE 5; Vn-BE 6; *cis*-PEE
 7; IBEE 8; styrene
 9; *p*-methoxystyrene

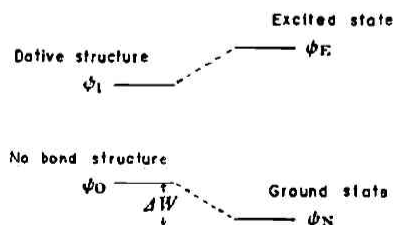


Fig. 5 Charge-transfer interaction diagram

$$\psi_N = a\psi_O(D, A) + b\psi_I(D^+ - A^-) \quad (1)$$

$$W_N \approx W_O - \frac{|H_{OI} - S_{OI}W_O|^2}{W_I - W_O} \quad (2)$$

$$\frac{b}{a} \approx \frac{H_{OI} - S_{OI}W_O}{W_I - W_O} \quad (3)$$

The energy of formation ΔW can be approximately written from Eqs. (2) and (3) as;

$$\begin{aligned}\Delta W &= W_s - W_0 \\ &\approx -\left(\frac{b}{a}\right)^2 (W_1 - W_0).\end{aligned}\quad (4)$$

Here, $W_1 - W_0$ is approximately equal to the CT transition energy $h\nu_{CT}$. Then, we have

$$\Delta W \approx -\left(\frac{b}{a}\right)^2 h\nu_{CT}. \quad (5)$$

When the donor molecules differ little in polarity, size, and polarizability with the acceptor fixed, the contribution of the conventional van der Waals force to the complex formation would not vary so much in the series. If so, the relative variation in ΔW by the substituent can be expressed as;

$$\begin{aligned}\partial \Delta W &= \Delta W - \Delta W^\circ \\ &\approx -\left(\frac{b}{a}\right)^2 h\nu_{CT} + \left(\frac{b^\circ}{a^\circ}\right)^2 h\nu_{CT}^\circ,\end{aligned}\quad (6)$$

where the superscript " $^\circ$ " indicates a reference compound. In the case of weak CT complexes the value of $\left(\frac{b}{a}\right)^2$ is almost constant in the series. Then, we have

$$\partial \Delta W \approx -\left(\frac{b^\circ}{a^\circ}\right)^2 h(\nu_{CT} - \nu_{CT}^\circ). \quad (7)$$

When we make the usual assumption that the variation in the equilibrium constant, K is mainly due to the change in the energy rather than due to the change in the entropy of formation, after all, we have from Eq. (7)

$$\ln K/K^\circ \approx \frac{1}{RT} \left(\frac{b^\circ}{a^\circ}\right)^2 h(\nu_{CT} - \nu_{CT}^\circ). \quad (8)$$

The fact that Eq. (8) is obeyed reasonably well in TCNE-ether complexes as seen in Fig. 4 does suggest that the variation in the value of K is almost due to that in the CT resonance energy¹⁷. The line C in Fig. 4 shows a similar relationship in molecular iodine (I_2)-alkyl vinyl ether complexes¹⁷. By the gradient of this line the value of b^2 can be estimated from Eq. (8): it is about $0.04a^2$ for TCNE-ether complexes and about $0.08a^2$ for I_2 -alkyl vinyl ether complexes. The obtained values of b^2 are in good agreement with those determined for some other CT complexes by IR or dipole moment measurement^{2,18}.

However, in the case of Ag^+ -unsaturated ether complexes¹⁸ the plot of $\log K$ vs. ν_{CT} has an inverse tendency, which would mean that the effect of β -methyl groups on the stability of Ag^+ complexes is negative on the contrary to that of TCNE complexes. This tendency could be interpreted by considering that the interaction distance between the donor and acceptor is much smaller than the sum of their van der Waals radii so that the steric hindrance of the β -methyl group may become important. In general the donor-acceptor distance in π - π complexes appears to be only slightly shorter than the sum of their van der Waals radii, while it is considerably shorter than that in the case of ν -acceptor, Ag^+ complexes and σ -acceptor, I_2 complexes. In addition, a similar phenomenon is observed in another case; the TCNE-olefin complexes studied here exhibit gradual increases in stability with increasing the double-bond substitution, in contrast with Ag^+ -olefin and I_2 -olefin complexes¹⁹ which become more unstable with

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18) T. Fueno, O. Kajimoto, T. Okuyama and J. Furukawa, *Bull. Chem. Soc. Japan*, **41**, 785 (1968)

the increase of substitution at the double bond.

It is found that the higher the NMR chemical shift of H_C in the corresponding donor, the larger the stability of the TCNE complex. Really, there are linear relationships between $\log K$ and τ value of H_C as seen in Fig. 6. The ^{13}C -NMR spectra reported by other authors²⁰⁾, ^1H -NMR spectra and the

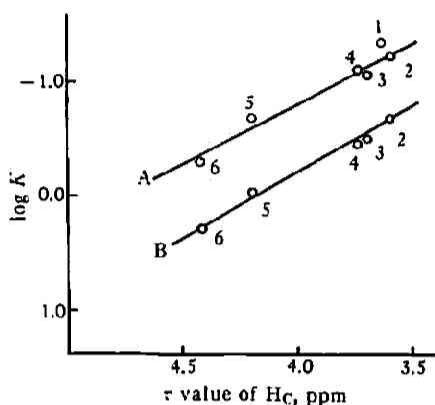


Fig. 6 A plot of $\log K$ vs. H_C chemical shift

A; at 30°C in CHCl_3

B; at 20°C in CCl_4

1; V2-CIEE 2; VME 3; VEE

4; Vi-BE 5; *cis*-PEE 6; IBEE

EHMO calculation described below show that π -electron density on the α -carbon (C_α) increases and that on C_β decreases as alkoxy groups become bulkier and the number of β -substituents increases. According to these facts, it could be supposed that the interaction of π -electron on C_α with TCNE is more important than the interaction of π -electron of C_β with TCNE in the complex formation.

Extended Huckel MO calculation

Method of calculation

As previously discussed the steric effect is less important in the initial complex formation. Thus the relative reactivity in the complex formation could be discussed mainly in terms of the electronic energy change between the initial stage and the complex stage. Such energy change may be approximately estimated by a MO method. In order to consider the effects of α - and β -substituents, σ -electronic system should be dealt with as well as π -system, and then the EHMO method developed by Hoffmann²¹⁾ was adopted here. All the calculations and parametrizations were performed according to the original prescription of Hoffmann. Since the geometry of each molecule except TCNE²²⁾ has not been established, a reasonable one was postulated with the usual bond lengths and angles²³⁾, although the C-O-C bond angle was arbitrarily assumed to be tetrahedral. The molecular geometry adopted

19) (a) R. J. Cvetanović, F. J. Duncan, W. E. Falconer and R. S. Irwin, *J. Am. Chem. Soc.*, **87**, 1827 (1965)

(b) R. J. Cvetanović, F. J. Duncan, W. E. Falconer and W. A. Sunder, *ibid.*, **88**, 1602 (1966)

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22) D. A. Bekoe and K. N. Traeblood, *Z. Kristallogr.*, **113**, 1 (1960)

23) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill (1970)

here for VEE is shown in Fig. 7.

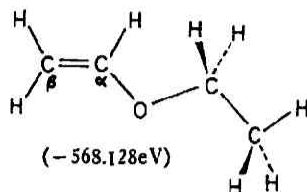


Fig. 7 The molecular geometry adopted here for VEE
The numerical value in the parenthesis is the
calculated total electronic energy.

Comparison with experiments

The electron population data given in Table 3 suggest that the electrophilic reactivity at C_β is

Table 3 Atomic population (AP) and π -atomic orbital population (π -AOP) on
the α - and β -carbons and oxygen of α , β -unsaturated ether

Donor	AP			π -AOP			HO, π -AOP			HOMO level, eV
	β - carbon	α - carbon	oxy- gen	β - carbon	α - carbon	oxy- gen	β - carbon	α - carbon	oxy- gen	
VEE	4.3590	3.4687	7.1632	1.1079	0.9209	1.9677	0.5472	0.4130	0.0351	-12.980
<i>trans</i> -PEE	4.1196	3.6135	7.1674	1.0097	1.0601	1.9725	0.3834	0.4675	0.0319	-12.503
<i>cis</i> -PEE	4.1184	3.6165	7.1620	1.0104	1.0607	1.9720	0.3851	0.4684	0.0308	-12.513
IBEE	3.9084	3.7308	7.1657	0.9322	1.1694	1.9757	0.3536	0.5239	0.0322	-12.248

reduced and, on the other hand, that at C_α is increased by the β -methyl substitutions. In fact, these population data on C_α coincide well with our experimental reactivity order for the complex formation; $VEE < trans\text{-}PEE < cis\text{-}PEE < IBEE$. This result supports the previous assumption that the role of π -electron on C_α is more significant than that on C_β in the complex. However, the total atomic population (AP) on C_β is far greater than that on C_α in contrast with the π -atomic orbital population (π -AOP) and the highest occupied π -atomic orbital population (HO, π -AOP). As π -electron certainly plays a dominant role in such π - π complexes, the π -AOP or HO, π -AOP would be one of the best reactivity indices for the complex formation. From the view point, however, we cannot examine the configuration of the complex. For this purpose it is a better method to estimate the delocalization energy for various kinds of configuration models shown in Fig. 8. The π -electronic delocalization energy for model (C) (ΔE_C) is approximately given by Eq. (9).

$$\begin{aligned} \Delta E_C &= 2 \left\{ \frac{\sum_i^{\text{occ}} \sum_j^{\text{unocc}}}{T} - \frac{\sum_i^{\text{occ}} \sum_j^{\text{unocc}}}{T} \right\} \frac{(C_\alpha^i C_\beta^j + C_\beta^i C_\alpha^j)^2}{E_i - E_j} (-\gamma^2) \\ &\approx 2 \sum_j^{\text{unocc}} \frac{1}{T} - \frac{(C_\alpha^i C_\beta^j + C_\beta^i C_\alpha^j)^2}{E_i - E_j} (-\gamma^2) \end{aligned} \quad (9)$$

where γ is the resonance integral between the component molecules being assumed for simplicity to be constant for any type of interaction. The values of ΔE for various configuration models are summarized in Table 4. Models (B), (C) and (E) adequately predict our experimental results. Among these three models, model (E) is in most reasonable agreement with Mulliken's "Overlap and orientation principle"²⁴⁾.

24) R. S. Mulliken, *Rec. Trav. Chim.*, 75, 845 (1956)

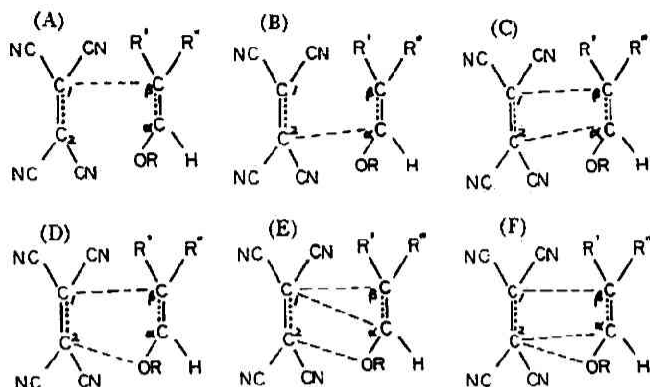
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Fig. 8 The configuration models for calculating the delocalization energies

Table 4 Calculated delocalization energies for the various configuration models

Donor	(A)	(B)	$4E_1 - \gamma^2/\text{eV}$ (C)	(D)	(E)	(F)
VME	0.0922	0.0692	0.0029	0.2332	0.4865	—
VEE	0.0922	0.0692	0.0029	0.2261	0.4869	0.1039
Vi-PE	0.0936	0.0716	0.0037	0.2340	0.4957	—
<i>trans</i> -PEE	0.0933	0.1061	0.0045	0.2482	0.5968	0.1021
<i>cis</i> -PEE	0.0930	0.1058	0.0046	0.2388	0.6056	0.0962
IBEE	0.0926	0.1427	0.0111	0.2487	0.5933	0.0917

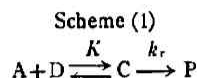
Before the kinetic experiments were carried out, we thought that this model was regarded as a good transition state model for the cycloaddition, and that the delocalization energy was an index of the activation energy. As discussed below, however, the steric effect is important to some degree in the process of the cycloaddition, and it is concluded that the reactivity indices derived from the EHMO method in which only the electronic energy change is considered cannot be applied to the successive cycloaddition.

Kinetics

A characteristic color due to the 1 : 1 CT complex appears immediately after mixing and gradually diminishes; during the change of the color, in NMR spectra only the reactant ether and the cycloadduct are observed and nothing else can be found. Just at the time the color completely disappears, the change in the NMR spectra stops. In this reaction process TCNE anion radical could not be detected²⁵⁾. Thus the cycloaddition accompanies no side reactions. The cycloaddition was followed by observing the CT band and the pseudo first order rate constant obtained by Guggenheim's plot was almost constant despite the different wave lengths near the CT maximum band. The second order rate constant, k_{11} is pseudo first order rate constant divided by the initial donor concentration (D); first order in the donor and in the CT complex respectively. The value of k_{11} decreases with the increase in (D) for

25) N. S. Isaacs, *J. Chem. Soc., B*, 1053 (1966)

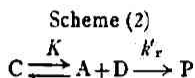
cis-PEE and IBEE, while it is independent of (D) for VEE, Vi-BE, VME and V2-CIEE within the experimental error. Dependence of k_{II} on the acceptor concentration is not found for all the systems in the concentration range from $7.0 \times 10^{-4} M$ to $3.5 \times 10^{-3} M$. Those phenomena can be satisfactorily interpreted by Scheme (1) or (2), though Rappoport *et al.*²⁶⁾ proposed Scheme (3) based on the similar



$$\frac{d(C)}{dt} = -\frac{k_r K(D)(C)}{1 + K(D)} \quad (1-1)$$

$$k_I = \frac{k_r K}{1 + K(D)} \quad (1-2)$$

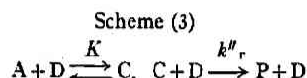
$$\frac{1}{k_I} = \frac{(D)}{k_r} + \frac{1}{k_r K} \quad (1-3)$$



$$\frac{d(C)}{dt} = -\frac{k'_r (D)(C)}{1 + K(D)} \quad (2-1)$$

$$k_I = \frac{k'_r}{1 + K(D)} \quad (2-2)$$

$$\frac{1}{k_I} = \frac{1}{k'_r} + \frac{K(D)}{k'_r} \quad (2-3)$$



$$\frac{d(C)}{dt} = -\frac{k''_r K(D)^2(C)}{1 + K(D)} \quad (3-1)$$

$$k_I = \frac{k''_r K(D)}{1 + K(D)} \quad (3-2)$$

$$\frac{1}{k_I} = \frac{1}{k''_r K(D)} + \frac{1}{k''_r} \quad (3-3)$$

kinetic study in the tricyanovinylolation of aromatic amines. Schemes (1) and (2) predict the decrease of k_{II} with the increase in (D) for *cis*-PEE and IBEE. On the other hand, in the case of Scheme (3) the increase in (D) must increase the value of k_{II} unless $K(D) \gg 1$; however $K(D)$ is not so larger than 1 for our systems. The value of k_{II} is independent of (D) for VEE etc. because $K(D) \ll 1$ in Eq. (1-2) or (2-2), and then $k_{II} = k_r K$ or k'_r , respectively. As discussed extensively by Andrews and Keefer²⁵⁾, however, the kinetic method alone does not enable us to distinguish between Scheme (1) in which the complex lies on the reaction co-ordinate and Scheme (2) in which the complex formation is a side reaction in a rapid equilibrium with free donor and acceptor. As expected from Eq. (1-3) or (2-3), the plot of $1/k_{II}$ vs. (D) has fairly good linearity for *cis*-PEE and IBEE as seen in Fig. 9. The rate

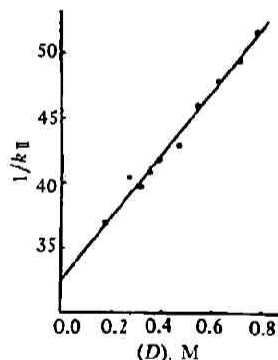


Fig. 9 A plot of $1/k_I$ vs. the initial donor concentration (D)
Donor: IBEE

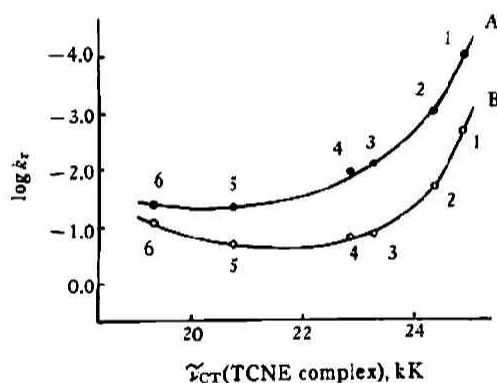
constants k_r , k'_r and initial association constant K are determined by the slope and intercept of the plot. The value of K obtained thus is found in good accordance with that previously determined by the B-H plot. The obtained kinetic parameters for both Schemes (1) and (2) are listed in Table 5.

As seen in the interesting plots of $\log k_r$ and k'_r against $\bar{\nu}_{CT}$ in Fig. 10, each curve is not linear with a shallow minimum in contrast with that of the complex formation (Fig. 4). There is an essential difference in the substituent dependence on the relative reactivity between in the cycloaddition and in the CT complex formation. Thus, the reactivity difference between the cycloaddition and the complex

26) Z. Rappoport and A. Horowitz, *J. Chem. Soc.*, 1348 (1964)

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Donor		10°C	20°C	30°C	E_a eV	ΔS^\ddagger eu
<i>cis</i> -PEE	k_r a)	1.0×10^{-1}	1.4×10^{-1}	2.3×10^{-1}	6.9	-41
	k'_r b)	2.5×10^{-2}	3.1×10^{-2}	4.1×10^{-2}	4.4	-52
IBEE	k_r	2.8×10^{-2}	4.7×10^{-2}	7.1×10^{-2}	8.2	-39
	k'_r	2.1×10^{-2}	3.1×10^{-2}	3.7×10^{-2}	5.2	-50
VEE	k_r	4.4×10^{-2}	6.8×10^{-2}	1.0×10^{-1}	7.3	-41
	k'_r	4.4×10^{-3}	6.4×10^{-3}	9.1×10^{-3}	6.8	-48
Vi-BE	k_r	—	—	1.5×10^{-1}		
	k'_r	—	—	1.1×10^{-2}		
VME	k_r	—	—	1.0×10^{-2}		
	k'_r	—	—	7.3×10^{-4}		
V2-CIEE	k_r	—	—	2.0×10^{-3}		
	k'_r	—	—	1.0×10^{-4}		

a) sec^{-1} b) $\text{M}^{-1}\text{sec}^{-1}$ c) kcal mol^{-1} d) e. u.Fig. 10 A plot of $\log k_r$ vs. the frequency of the CT band for some TCNE complexesA: $\log k'_r$ B: $\log k_r$ 1: V2-CIEE 2: VME 3: VEE
4: Vi-BE 5: *cis*-PEE 6: IBEE

formation seems not to be explained concurrently merely in terms of the electronic structure of the ground state of the reactant ethers; likely the chemical non-crossing rule²⁷⁾ cannot be assumed in this type of cycloadditions. In order to explain the implication of the negative slope of the plots for *cis*-PEE and IBEE in Fig. 10, some steric effect is to be taken account of in addition to the electronic effect as in the case of Ag^+ -unsaturated ether complexes described before. The activation entropy of the cycloaddition is very large negative; *ca.* -40 e. u. in Scheme (1) and *ac.* -50 e. u. in Scheme (2), while the entropy of the complex formation is *ca.* -10 e. u. Then, it seems that the configuration between the donor and acceptor in the transition state is so rigid that the steric effect overshadows the electronic effect of β -methyl groups, while in the complex state the configuration is so labile that the electronic effect is more significant than the steric effect.

Next we studied the stereochemistry of the cycloaddition of TCNE with PEE in the isomer range 96-30% of *cis*-PEE in CH_2Cl_2 . The reactant isomer composition was determined by vapor phase chromatography and NMR. The product isomer composition was determined by NMR characteristic absorption intensities: *cis*-adduct: $\tau=6.3$ (H_A) and $\tau=5.0$ (H_C); *trans*-adduct: $\tau=6.6$ (H_B) and $\tau=$

27) R. D. Brown, *Quart. Rev.*, **6**, 63 (1952)

5.3 (H_C). The reactant isomer composition is always equal to the product isomer composition in each run. This result suggests that the cycloaddition is stereoselectively *cis*, in other words, it will follow $2\pi s + 2\pi s$ approach.

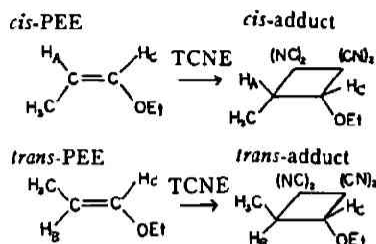


Fig. 11 Stereochemistry of the cycloaddition reaction

Why is the unsaturated ether "REACTIVE" and is the olefin "NONREACTIVE" as shown in Table 1, though two kinds of the donors have similar CT bands and NMR spectra? This reactivity difference should mainly be attributed to considerable transition state stabilization of the TCNE-ether system. The transition state of the TCNE-olefin system is isoconjugate to antiaromatic cyclobutadiene when $2\pi s + 2\pi s$ approach is followed. Similarly, the transition state of the TCNE-ether system is isoconjugate to cyclobutadiene in the same approach. In the former case resonance does not reduce the antiaromaticity of cyclobutadiene, while in the latter case resonance can effectively destroy the antiaromaticity as seen in Fig. 12. This presumption is supported by the fact that "Push-Pull" cyclobutadiene is isolated stably²⁸⁾.

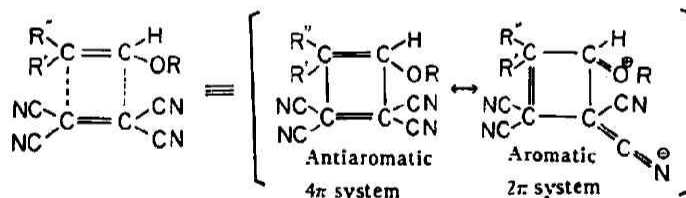


Fig. 12 The transition state of $2\pi s + 2\pi s$ cycloaddition for the TCNE-ether system

Correlation diagram

$2\pi s + 2\pi s$ thermal cycloaddition is symmetrically forbidden from the Woodward-Hoffmann rule²⁹⁾. Why does our cycloaddition proceed under very mild conditions in this pathway? In order to consider this question we prepared the molecular orbital correlation diagrams for two cases. Fig. 13 shows the correlation diagram for a typical $2\pi s + 2\pi s$ non-polar cycloaddition *i. e.* ethylene-butene-2 system. The energy levels of the MO's of the cycloaddends and the transition state (TS) complex have been determined by reference to ionization potential and ultraviolet spectroscopy and also by the EHMO calculation. Moreover, Fig. 14 shows the correlation diagram for a typical $2\pi s + 2\pi s$ polar cycloaddition

28) (a) Von R. Gompper and G. Seybold, *Angew. Chem.*, **80**, 804 (1968)

(b) M. Neuenschwander and A. Niederhauser, *Helv. Chim. Acta*, **53**, 519 (1970)

29) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, London (1970)

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i. e. IBEE-TCNE system. We will compare these two diagrams. First, the diagram in Fig. 13 shows that the lowest state of the TS complex correlates with a diexcited cyclobutane product and accordingly the reaction is thermally forbidden. In order to render the reaction allowed in $2\pi s + 2\pi s$ approach two electrons must be promoted from ψ_2 to ψ_3 . This would need the expenditure of considerable energy since the energy gap between ψ_2 and ψ_3 can be estimated to be 4.5 eV. Such a considerably much energy is not supplied by means of thermal agitation, and then a non-polar $2\pi s + 2\pi s$ thermal cycloaddition cannot proceed. Secondly, the diagram in Fig. 14 shows the same shape as before and the reaction is formally not allowed. Unlike the previous case, however, the promotion of two electrons from ψ_2 to ψ_3 would require only small energy expenditure since its energy gap is very small; *ca.* 1 eV. Hence a polar $2\pi s + 2\pi s$ thermal cycloaddition may well occur under mild conditions.

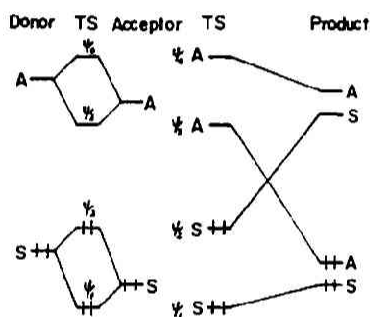


Fig. 13 The correlation diagram for a suprafacial non-polar $2\pi + 2\pi$ approach

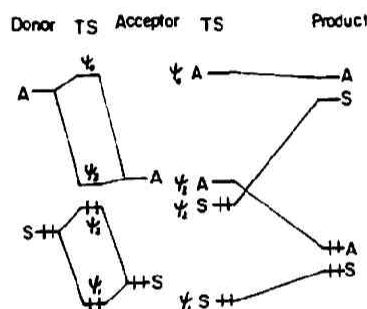


Fig. 14 The correlation diagram for a suprafacial polar $2\pi + 2\pi$ approach

Acknowledgments

The authors wish to thank Dr. M. Sasaki, Dr. M. Nakahara and Mr. F. Tanaka for their helpful discussions and suggestions.

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